With a grain of salt

Boer, P.K. de; Groot, R.A. de

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P.K. de Boer [1], R.A. de Groot

Electronic Structure of Materials, Research Institute for Materials, Toernooiveld 1, 6525 ED, Nijmegen, The Netherlands

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Abstract

Electronic structure calculations on sodium chloride are reported. It is shown that the conduction band has a predominant chlorine character, contrary to the common picture of the conduction band being derived from sodium states.

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The electronic structure of alkali halides like table salt (NaCl) can be found in any freshman's textbook. One electron is transferred from sodium to chlorine, the occupied chlorine 3p states form the valence band, while the empty sodium states hybridise into a conduction band. Alkali halides are considered as the archetypes of compounds having a charge transfer gap, i.e. compounds where the wave function character of the highest occupied state is determined by the anion, while the wave function of the lowest unoccupied state is associated with the cation. Unfortunately this intuitive picture turns out to be wrong.

While we agree on the description of the valence band, we would like to point out that this picture of the conduction band is incorrect even in first order of approximation. The conduction band is actually a wide free electron-like band. Such a band can be interpreted of course in terms of atomic wave functions, but by doing so, it turns out that the predominant character of the bottom of the conduction band is of chlorine character as well, because the chlorine 4s levels are positioned well below the sodium levels.

We calculated the electronic structure of NaCl with the Full Potential Linearized Augmented Plane Wave (FLAPW) method [1]. This method is based upon Density Functional Theory with the exchange-correlation energy treated within the Local Density Approximation (LDA). In order to give an analysis of the conduction bands in terms of atomic wave functions the calculations were repeated with the Localized Spherical Wave (LSW) method [2], which, besides LDA, employs the Atomic Sphere Approximation (ASA). The calculations with the LSW method and the FLAPW method resulted in the same

[1] Tel: +31 (0)24 3652810, Fax: +31 (0)24 3652120, E-mail: peterdb@sci.kun.nl

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band structure which assures the reliability of the ASA approximation. The application of LDA is justified as well. The main effect of LDA here is a rigid shift of the valence bands with respect to the conduction bands, which leads to band gaps which are too small compared with experimental values but which has no important consequences for the topology and the wave function character of the bands.

How various atomic states influence the conduction band is shown in the the Fig. 1. The top panel shows the calculated band structure of NaCl. The middle panel depicts the band structure in a calculation where the sodium is removed altogether (fcc chlorine with the lattice parameter of NaCl). Hardly any differences are visible. The bottom panel shows the band structure with chlorine 4s states removed from the calculation. The topology of the conduction band is fundamentally different in this case. For example the gap is indirect, in disagreement with experiment.

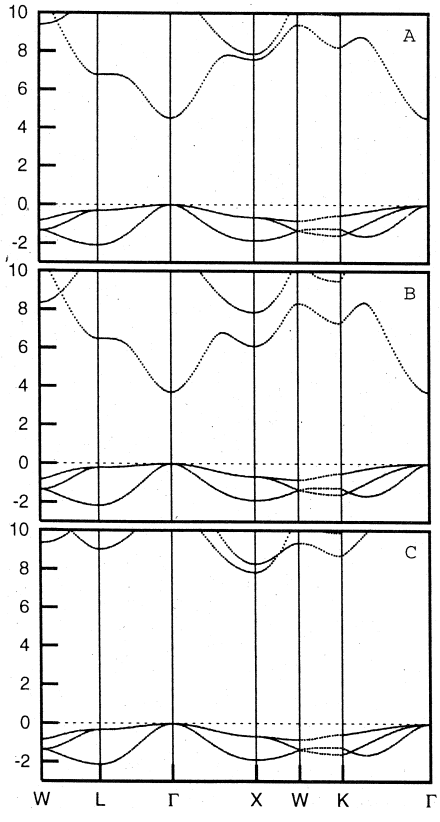

Fig. 1. The calculated bandstructure of NaCl. Energy scale in eV. Shown are the valence bands and lowest conduction bands of (A) NaCl, (B) Hypothetical fcc Cl^-, and (C) NaCl without Cl-4s states.

Table 1
Experimental gaps of alkali halides (in eV) (from Ref. [3])

	F	Cl	Br
Li	13.6	9.4	7.6
Na	11.6	8.5	7.5
K	10.7	8.4	7.4
Rb	10.3	8.2	7.4
Cs	9.9	8.3	7.3

This finding has several consequences. First, alkali halides do not have a charge transfer gap. The situation in NaCl should not be confused with covalency, which deals with the hybridisation of states on different atoms. Its effects are most pronounced in a situation where the highest occupied states and the lowest unoccupied states reside on dissimilar atoms. This is not the case in NaCl.

Second, since the top of the valence band and the bottom of the conduction band are positioned on the anion, one expects the band-gap to be determined by the anion and to be independent of the cation in first approximation. This is actually the case as it can be seen in the Table 1, which lists experimentally determined band gaps [3]. The weak dependence of the gap on the cation shows the influence of the cation on the band widths of both valence and conduction bands, primarily through its influence on the lattice parameter.

Similar conclusions are valid for the currency-metal halides like AgCl. Here the valence band is more complicated because of the presence of metal d states, leading to a valence band maximum at L in the Brillouin zone. The conduction band, however, is primarily derived from anion states. Direct experimental evidence for the chlorine contribution to the conduction band exists here [4]. This different interpretation of the electronic properties of AgCl can have important consequences for the explanation of photographic processes.

It is interesting that the importance of the anion character for the conduction band was correctly emphasized in one of the first papers on NaCl more than half a century ago [5]. This work is part of the research program of the Stichting voor Fundamenteel

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